Acrylic acid nitrile, a film-forming electrolyte component for lithium-ion batteries, which belongs to the family of additives containing vinyl groups

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Abstract

We present results on the electrolyte additive acrylic acid nitrile (AAN), which allows the use of propylene carbonate (PC)-based electrolytes together with graphitic anodes. This report will focus on the basic electrochemical properties and on XPS results of the films formed in the presence of AAN. Further data on in situ investigations of AAN is presented in another paper of this proceedings. The combination of both reports gives strong evidence, that the initiative step for solid electrolyte interphase (SEI) formation is a cathodic, i.e. by reduction induced electro-polymerisation of the vinyl-group. It is concluded that this electro-polymerisation may also be a main reduction mechanism of other vinyl compounds such as vinylene carbonate (VC), vinylene acetate and others.
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Keywords: Electrolyte additive; Solid electrolyte interphase (SEI); Acrylic acid nitrile; Electrochemical polymerisation; Lithium-ion battery

1. Introduction

Liquid non-aqueous solvents have found numerous applications in liquid and liquid/polymer hybrid electrolytes for lithium batteries [1–3]. The choice of solvents or solvent mixtures for a certain lithium-ion battery application is usually a compromise between the desired physical (e.g. electrolyte conductivity, volatility, flammability, wetting ability, etc.) and electrochemical properties (reduction and oxidation at the respective electrode/electrolyte interfaces, solid electrolyte interphase (SEI) formation behaviour, etc.) [4]. An elegant way to overcome the inevitable limitations of this compromise is the use of electrolyte additives, which even in small amounts ("additive amounts") improve the electrolyte properties in the desired direction [4]. The technological realisation of this concept is quite simple, as the electrolyte additive can be just added to the base electrolyte. Among many additive applications, such as overcharge protection and cell safety improvement, electrolyte additives for improved film formation processes at anode and cathode have found particular interest.

There is by far more information available on electrolyte additive effects at the anode interface than at the cathode interface. At the graphitic carbon anode side, the first reports deal with gaseous electrolyte additives such as CO_2 [5–10], N_2O [6,7] and SO_2 [6,11,12]. Some other prominent examples are derivative or analogous compounds of the cyclic carbonates ethylene carbonate (EC) and propylene carbonate (PC), e.g. chloro ethylene carbonate [13] (which evolves CO_2 during reduction [14,15]), fluoro ethylene carbonate [16], ethylene sulfite [4,17], propylene sulfite [18] and vinylene carbonate (VC) [19]. Also derivative or analogous compounds of the linear carbonate diethyl carbonate (DEC) and dimethyl carbonate (DMC), e.g. dimethyl sulfite and diethyl sulfite [17,20], *S,S*-dialkyl dithiocarbonates [21], ethyl propyl carbonate [22], ethyl methyl carbonate [23,24] and other asymmetric alkyl methyl carbonates [25] have been proven to be useful. A third family of compounds include partially halogenated organic compounds such as bromo butyrolactone [26], chloro or fluoro ethylene carbonate (see above) and fluorinated non-cyclic compounds as glycol ethers [27], urethanes [28], glycol esters [29] as well as *N,N*-dimethylamino trifluoroacetamide [30,31].

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Apart from the quality of the formed films, these compounds take advantage from the fact that they are usually reduced at quite positive graphite electrode potentials, i.e. at the early stages of the first reduction of the graphite electrode. This sensitiveness towards reduction may be for instance explained (i) by the electron-withdrawing effect of the chlorine- or fluorine-containing functional group introducing partial positive charge on the molecule (chloro ethylene carbonate, fluorinated solvents) or (ii) by the presence of atoms or groups in the structural formula which have a high electron affinity, e.g. sulfur in the oxidation state +IV (sulfites) or double bonds (vinylene carbonate).

In many cases, this sensitiveness to reduction allows the use of propylene carbonate-based electrolytes. PC exposes a large liquid range from $-49\,^{\circ}C$ to $+240\,^{\circ}C$ and has high ability for ion dissociation. Thus, PC based electrolytes usually show a low temperature performance desired for use in lithium-ion cells. Unfortunately, PC is a typical example for an electrolyte solvent which tends to co-intercalate into graphite, resulting in detrimental graphite exfoliation. The addition of an electrolyte additive, which forms a protecting film before solvated intercalation can take place, is a viable way for the application of PC together with highly graphitic anodes.

In this contribution, we present results on the novel electrolyte additive acrylic acid nitrile (AAN, often also named acrylonitrile) [32,33]. This additive belongs to the large family of vinylene compounds, where well known additives, such as vinylene carbonate [19] and vinylene acetate [34] stem from, too.

2. Experimental

Propylene carbonate and dimethyl carbonate (Merck and Honeywell, battery grade), $LiClO_4$ (Mitsubishi Chemical Corp., battery grade) and acrylic acid nitrile (Aldrich) were used as received. Graphite based anodes were made from TIMREX® SFG 44 and KS 6 synthetic graphites (Timcal AG). In order to prepare the electrodes, a slurry of the respective graphite suspended in a solution of poly(vinylidene)fluoride (PVdF) (Aldrich) in 1-methyl-2 pyrrolidinone (Aldrich) was spread on a stainless steel current collector, dried at $120\,^{\circ}C$ overnight, then pressed at $100\,kg\,cm^{-2}$, and finally dried under vacuum at $120\,^{\circ}C$ for 4 h again. The electrodes contained 4 wt.% of PVdF binder.

$LiMn_2O_4$ based cathodes were made from 90 wt.% $LiMn_2O_4$ (Allied Signal), 6 wt.% carbon black (Printex L6, Degussa), and 4 wt.% PVdF. The preparation of the cathodes was carried out as described for the anodes, but instead of steel, titanium mesh was used as current collector.

Electrolyte preparation and cell assembly were accomplished under dry argon atmosphere in a glove box. The water content of the electrolytes determined by Karl Fischer titration was less than 15 ppm. Electrochemical experiments were carried out in laboratory type glass cells with bulk lithium counter and reference electrodes and an excess of electrolyte. The electrodes were not closely packed in separator materials but placed in the electrolyte without any further support or protection. Current densities and specific charges are given with respect to the masses of active material.

The X-ray photoelectron spectroscopy (XPS) measurements were performed with a PHI 5400 electron spectrometer, using unmonochromated Mg Kα radiation ($hv = 1253.6\,eV$). The samples consisted of highly graphitic carbon fibers P100 (Amoco) and were analysed after the first charge/discharge cycle. After removal from the cell, the samples were washed with DMC and then dried in vacuum overnight at room temperature. Special sample holders warranted that the cycled fibers were not exposed to air during transfer from the electrochemical cell to the XPS chamber. XPS spectra were collected after different sputtering times in order to get a depth profile of the SEI.

3. Results and discussion

Pure PC-based electrolytes are not compatible with graphite anodes, due to solvent co-intercalation into the graphite matrix, subsequent electrolyte reduction and strong gas evolution inside the graphite matrix, resulting eventually in strong graphite exfoliation [35]. The situation completely differs when only 1 vol.% acrylic acid nitrile (AAN) is added to the electrolyte (Fig. 1). Cyclic voltammetry illustrates that the film formation reaction at approximately 1.3 V versus Li/Li^+ is sparsely current consuming and the co-intercalation of PC is effectively suppressed. Unsolvated reversible lithium intercalation is possible. In the second cycle, the reaction at 1.3 V versus Li/Li^+ is not visible anymore indicating that the filming process is more or less completed.
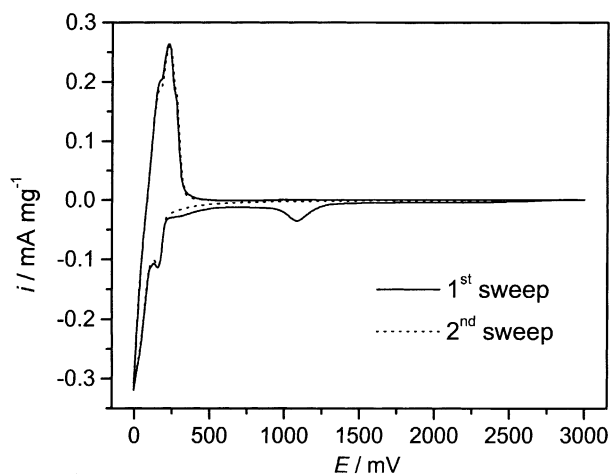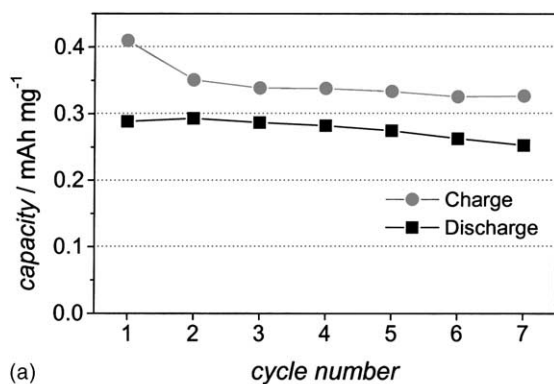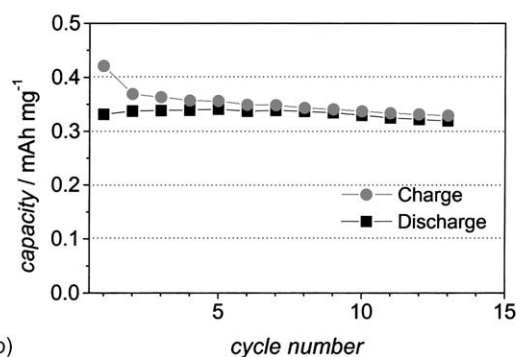

Fig. 1. First (solid line) and second (dashed line) cyclic voltammograms of synthetic graphite TIMREX® KS 6 in 1 M $LiClO_4$ in PC:AAN (99:1, v:v). Scan rate = $0.05\,mV\,s^{-1}$.

Fig. 2. (a) Constant current charge cycling of graphite (TIMREX® SFG 44) in 1 M LiClO$_4$ in PC:AAN (99:1, v:v) with a constant current of ±20 mA g^{-1}, cut-off: 0.02/1.5 V vs. Li/Li$^+$. The efficiency was 70% in the first cycle, and <85% in the following cycles; (b) same graphite and electrolyte, but different charging process: potentiodynamic ramp from 3.0 to 0.5 V vs. Li/Li$^+$ in the first charge, then constant current cycling at ±20 mA g^{-1}, cut-off: 0.02/1.5 V vs. Li/Li$^+$ in the rest of the first cycle and subsequent cycles. The efficiency was >80% in the first cycle and ⩾90% in the following cycles.

Fig. 3. "Plating" of SEI film products on the anode. Composition and morphology of the SEI deposit are controlled by the "plating conditions", i.e. by (i) the electrolyte composition, in particular the relative amount of the respective SEI forming electrolyte component; (ii) the pretreatment of the surface; and (iii) the plating conditions (constant current or pulse plating, etc.). (a) Plating conditions, favoring nucleation, result in a compact and dense SEI; (b) plating conditions, which facilitate the crystal growth of the initially formed nuclei, induce the formation of a rough SEI deposit, which requires more SEI products to get pin-hole-free, i.e. consumes more irreversible capacity. In general, these considerations can be considered to be valid for anode and cathode (taken from [36]).

A very important finding was, that the type of charge procedure in the first cycle obviously has a substantial impact on the SEI formation process. Fig. 2 reveals that the efficiency (= ratio of discharge to charge capacity) in the first and in the later cycles can be very much improved, when constant current charging is replaced by a charge program involving a potentiodynamic and galvanostatic step. This may be associated with differences in the SEI formation processes (Fig. 3).
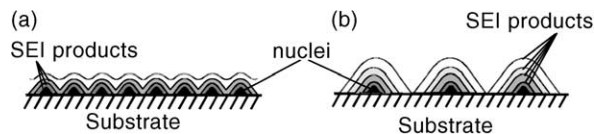
XPS is a useful tool to investigate SEI products and moreover argon sputtering allows to obtain a depth profile of the SEI. Longer sputtering times reveal the inner SEI parts to the XPS beam. This means, "inner SEI" products, which have been formed in contact to the carbon surface, can be distinguished from "outer SEI products", which are farther away from the carbon surface. The relative elemental surface composition of graphitic carbon fibres cycled in 1 M LiClO$_4$ in PC without and with the additive AAN is shown in Table 1. As expected, the SEI is heterogeneous and the respective SEI products vary in quality and quantity across the width of the SEI. Nitrogen could only be found in the SEI of the fibre, which was cycled in the presence of AAN. The presence of Cl in the SEI witnesses that the electrolyte salt LiClO$_4$ is also involved in the SEI formation process. Different parts of the film contain Cl in different oxidation states. Near the carbon surface, i.e. after sputtering, the predominant oxidation state of Cl is −I, indicating a reduction of the electrolyte salt. In the outer SEI parts, i.e. before sputtering, the predominant oxidation state of Cl is +VII (Fig. 4 and Table 1), indicating (i) the incorporation of LiClO$_4$ in the SEI or (ii) rests of the electrolyte which are stuck on the surface or penetrate in the pores of the SEI. It should be noted, that the samples were held over a considerable period of time under vacuum (not only after removal from the electrochemical cell, but also before and

Table 1
XPS data (before and after sputtering) of the SEI formed on highly graphitic carbon fibres P100 (Amoco) after the first charge/discharge cycle in 1 M LiClO$_4$ in PC as electrolyte with and without the electrolyte additive AAN (2 vol.%)

Sputter time (min)	Fibre in 1 M LiClO$_4$/PC			Fibre in 1 M LiClO$_4$/PC:AAN (98:2, v:v)		
	0 (%)	5 (%)	10 (%)	0 (%)	5 (%)	10 (%)
C 1s	49.2	36.4	29.0	61.3	41.6	36.3
O 1s	28.6	30.5	30.6	23.1	21.7	21.9
Cl 2p (Cl^{-I})	2.0	8.8	12.4	1.4	14	16
Cl 2p (Cl^{+VII})	2.6	0.9	<0.6	2.6	<0.5	<0.3
Li 1s	17.6	23.4	27.3	11.7	20.4	23.7
N 1s	–	–	–	–	2.1	1.9

The electrochemical experiments were performed according to the charge program denoted in Fig. 2b.
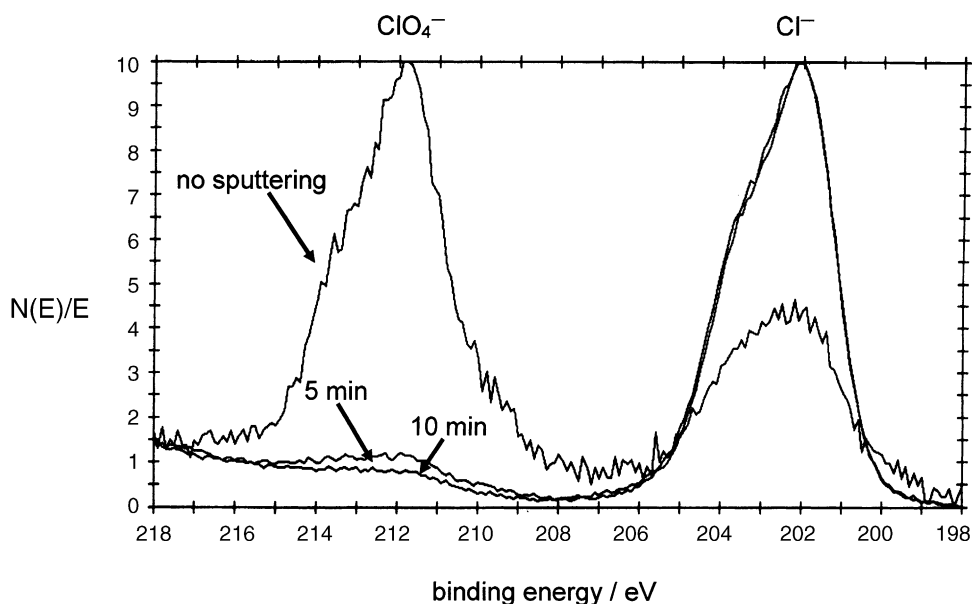
Fig. 4. Detail of the XPS spectra (Cl 2p), showing the change of bond type (or in other words, the change of the Cl oxidation state) with increasing sputtering times.
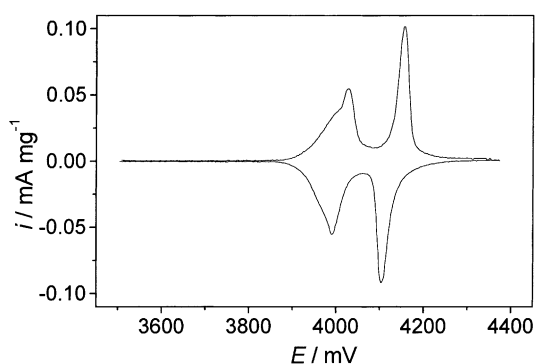

Fig. 5. Voltammograms of the 1 M LiClO$_4$/PC:AAN (99:1, v:v) electrolyte, showing the oxidation behaviour at LiMn$_2$O$_4$ (Allied Signal) v: 0.05 mV s^{-1}. Similar results have been obtained with LiN(SO$_2$CF$_3$)$_2$ as electrolyte salt.

during the measurement in the ultra high vacuum XPS chamber). Hence, only the less volatile SEI and electrolyte products remained in the SEI, which has been investigated by XPS.

In addition to its beneficial film forming behaviour on graphite, the 1 M LiClO$_4$/PC:AAN (99:1) electrolyte allows the use of "4 V" cathodes due to its oxidation stability and/or the formation of a protective cathode/electrolyte interface. Voltammetric measurements at a LiMn$_2$O$_4$ electrode verify an electrochemical window sufficient for operation in lithium-ion batteries (Fig. 5).

4. Conclusions

Acrylic acid nitrile is a useful film-forming electrolyte additive for lithium-ion batteries with graphitic anodes. PC

co-intercalation into graphite is suppressed in the presence of even small amounts of AAN. From the point of view of irreversible capacities, combined potentiodynamic and constant current charge in the first cycle is very much superior to simple constant current charge, which may be explained by a more favourable SEI formation ("SEI-plating") process. Also the oxidation behaviour of the additive-containing electrolyte is satisfactory. XPS proves that reduction products of AAN are included in the SEI.

We propose (and have also some strong evidence [37]), that AAN reduction and electrochemical polymerisation of the vinyl group is the initiative reaction for SEI formation. Electro-polymerisation reactions of vinyl groups are well known in electro-organic chemistry [38]. A general reaction scheme for reductive electro-polymerisation can be formulated according to Fig. 6a. This mechanism may also be valid for other vinyl compounds such as vinylene carbonate, vinylene acetate and others. Electron-withdrawing groups, –X, such as –CN, make the vinyl group more electrophilic and thus facilitate reduction, which is useful in combination with graphitic anodes as the SEI formation process can be finished before solvent co-intercalation takes place. On the other hand, electron-pushing groups, –Y, introduce a more nucleophilic character to the double bond and thus facilitate oxidation (cf. Fig. 6b), which can be a viable way to protect the cathode interface properly. In both cases, apart from electro-polymerisation of the vinyl-group, other subsequent and/or parallel reductive or oxidative reactions can not be excluded. For instance, an intermediate radical cation or anion (Fig. 6) may react with a PC molecule or ClO$_4^-$-anion nearby instead of reacting with another vinyl compound. As a consequence, "mixed" SEI products can be formed. These deliberations are generally valid, not only for vinyl compounds in 1 M LiClO$_4$/PC electrolytes, but also for
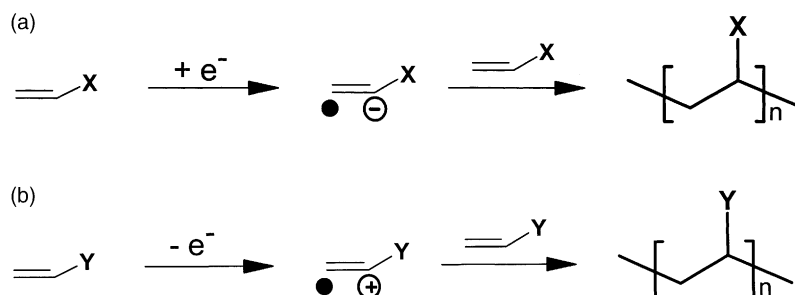
Fig. 6. (a) Cathodic, i.e. by reduction induced polymerisation of vinylene monomers. When the functional group "X" in α-position to the vinylene group is electron-withdrawing, reduction of the vinylene group is facilitateded; (b) anodic, i.e. by oxidation induced polymerisation of vinylene monomers. When the functional group "Y" in α-position to the vinylene group is electron-pushing, oxidation is promoted.

other multi-component electrolyte system. Moreover, these deliberations are also a reasonable explanation for the in most cases very heterogeneous composition of the SEI.

Acknowledgements

References

[1] J. Yamaki, S. Tobishima, in: J.O. Besenhard (Ed.), Handbook of Battery Materials, Part III, Wiley, Weinheim, 1999 (Chapter 3).
[2] J. Barthel, H.J. Gores, in: J.O. Besenhard (Ed.), Handbook of Battery Materials, Part III, Wiley, Weinheim, 1999 (Chapter 7).
[3] F.M. Gray, M. Armand, in: J.O. Besenhard (Ed.), Handbook of Battery Materials, Part III, Wiley, Weinheim, 1999 (Chapter 8).
[4] G.H. Wrodnigg, J.O. Besenhard, M. Winter, J. Electrochem. Soc. 146 (1999) 470.
[5] J.O. Besenhard, P. Castella, M.W. Wagner, Mater. Sci. Forum 91–93 (1992) 647.
[6] M. Winter, Diploma Thesis, University of Münster, Germany, 1993.
[7] J.O. Besenhard, M.W. Wagner, M. Winter, A.D. Jannakoudakis, P.D. Jannakoudakis, E. Theodoridou, J. Power Sources 43–44 (1993) 413.
[8] D. Aurbach, Y. Ein-Eli, O. Chusid, Y. Carmeli, M. Babai, H. Yamin, J. Electrochem. Soc. 141 (1994) 603.
[9] Y. Ein-Eli, B. Markovsky, D. Aurbach, Y. Carmeli, H. Yamin, S. Luski, Electrochim. Acta 39 (1994) 2559.
[10] J.O. Besenhard, M. Winter, J. Yang, International Workshop on Advanced Batteries, Lithium Batteries, Osaka, 1995, p. 129.
[11] J.O. Besenhard, M. Winter, J. Yang, W. Biberacher, J. Power Sources 54 (1995) 228.
[12] Y. Ein-Eli, S.R. Thomas, V.R. Koch, J. Electrochem. Soc. 144 (1997) L195.
[13] Z.X. Shu, R.S. McMillan, J.J. Murray, J. Electrochem. Soc. 142 (1995) L161.
[14] M. Winter, P. Novàk, J. Electrochem. Soc. 145 (1998) L27.
[15] M. Winter, F. Joho, R. Imhof, P. Novák, J. Power Sources 81–82 (1999) 818.
[16] R. McMillan, H. Slegr, Z.X. Sho, W. Wang, J. Power Sources 81–82 (1999) 20.
[17] G.H. Wrodnigg, C. Reisinger, J.O. Besenhard, M. Winter, ITE Batt. Lett. 1 (1) (1999) 111.
[18] G.H. Wrodnigg, T.M. Wrodnigg, J.O. Besenhard, M. Winter, Electrochem. Commun. 1 (1999) 148.
[19] M. Fujimoto, M. Takahashi, K. Nishio, Sanyo, US Pat. No. 5,352,548 (1994);
B. Simon, J.-P. Boeve, SAFT, US Pat. No. 5,626,981 (1997);
J. Barker, F. Gao, US Pat. No. 5,712,059 (1998);
Y. Naruse, S. Fujita, A. Omaru, US Pat. No. 5,714,281 (1998).
[20] G.H. Wrodnigg, J.O. Besenhard, M. Winter, J. Power Sources 97–98 (2001) 592.
[21] Y. Ein-Eli, S.F. McDevitt, J. Solid State Electrochem. 1 (1997) 227.
[22] Y. Ein-Eli, S. McDevitt, D. Aurbach, B. Markovsky, A. Schechter, J. Electrochem. Soc. 144 (1997) L180.
[23] H. Nakamura, H. Komatsu, M. Yoshio, J. Power Sources 62 (1996) 219.
[24] Y. Ein-Eli, S.R. Thomas, V. Koch, D. Aurbach, B. Markovsky, A. Schechter, J. Electrochem. Soc. 143 (1996) L273.
[25] Y. Ein-Eli, S.F. McDevitt, R. Laura, J. Electrochem. Soc. 145 (1998) L1.
[26] D. Billaud, A. Naji, P. Willman, in: Proceedings of the 9th International Meeting on Lithium Batteries, Poster TUES 7, Edinburgh, UK, 1998 (Abstracts).
[27] J.O. Besenhard, K.v. Werner, M. Winter, US Patent No. 5,916,708 (1997).
[28] W.K. Appel, J.O. Besenhard, S. Pasenok, M. Winter, G.H. Wrodnigg, German Patent DE 19,724,709 (1998).
[29] W.K. Appel, J.O. Besenhard, L.H. Lie, S. Pasenok, M. Winter, German Patent DE 19,858,924 (1998).
[30] W.K. Appel, J.O. Besenhard, L.H. Lie, S. Pasenok, M. Winter, German Patent DE 19,858,925 (1998).
[31] K.-C. Möller, T. Hodal, W.K. Appel, M. Winter, J.O. Besenhard, J. Power Sources 97–98 (2001) 595.
[32] K.-C. Möller, S.C. Skrabl, M. Winter, J.O. Besenhard, in: Proceedings of the 3rd Hawaii Battery Conference, Hawaii, USA, 2001, p. 228.
[33] K.-C. Möller, H.J. Santner, J.O. Besenhard, M. Winter, in: Proceedings of the 4th Hawaii Battery Conference, Hawaii, USA, 2002, p. 238.
[34] M. Yoshio, H. Yoshitake, K. Abe, T. Umeno, K. Fukuda, in: Proceedings of the 11th International Meeting on Lithium Batteries, Abstract No. 9, Monterey, CA, 2002.
[35] M. Winter, G.H. Wrodnigg, J.O. Besenhard, W. Biberacher, P. Novák, J. Electrochem. Soc. 147 (2001) 2427.
[36] H. Buqa, P. Golob, M. Winter, J.O. Besenhard, J. Power Sources 97–98 (2001) 122.
[37] K.-C. Möller, H.J. Santner, W. Kern, S. Yamaguchi, J.O. Besenhard, M. Winter, J. Power Sources (2002).
[38] J.W. Breitenbach, O.F. Olaj, F. Sommer, Adv. Polym. Sci. 9 (1972) 47.